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(54) Optical signal amplifier glasses.

(57) An optical signal amplifier comprising an optical waveguide fiber integrated by thallium ion exchange in a boron-free silicate glass doped with up to 5 weight % erbium oxide, the glass having a base composition, as calculated in weight percent on an oxide basis, consisting essentially of

SiO ₂	38-67	Al ₂ O ₃	1.5-4.5
Na ₂ O	0-20	ZnO	1.5-8
K ₂ O	0-25	Li ₂ O	0-1
Na ₂ O + K ₂ O	15-30	PbO	0-37
BaO	0-7	P ₂ O ₅	0-10
		P ₂ O ₅ + PbO	5-37

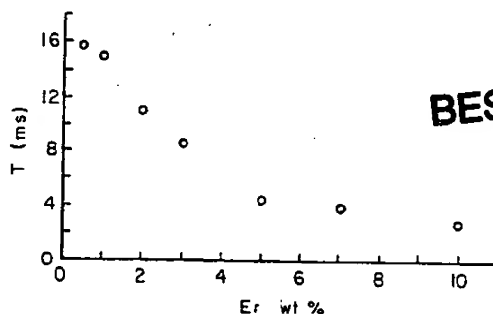


Fig. 1

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SiO ₂	38-67	Al ₂ O ₃	1.5-4.5
Na ₂ O	0-20	ZnO	1.5-8
K ₂ O	0-25	Li ₂ O	0-1
Na ₂ O + K ₂ O	15-30	PbO	0-37
BaO	0-7	P ₂ O ₅	0-10
		P ₂ O ₅ + PbO	5-37

10 BRIEF DESCRIPTION OF THE DRAWING

FIGURES 1 and 2 in the accompanying drawing are graphical representations of relevant properties measured on glasses in accordance with the present invention.

15 DESCRIPTION OF THE INVENTION

The present invention provides a family of glasses having general utility, particularly in lighting, optical and electronic applications. However, the glasses have unique features that render them of particular value in the production of an integrated, optical waveguide signal amplifier.

One feature of the present glasses is their freedom from boric oxide (B₂O₃). As explained earlier, it has been known that B₂O₃ exerts a very strong degrading effect on the spectroscopic effects in a glass doped with a rare earth metal oxide. However, B₂O₃ is commonly used for its beneficial effects on coefficient of thermal expansion and temperature-viscosity relationship in silicate glasses. The constituents of the present glasses are so proportioned that B₂O₃ is unnecessary and is omitted.

A further feature of the present glasses is their ability to be doped with relatively large amounts of erbium oxide (Er₂O₃). In the absence of B₂O₃ in the base glass, such doping has been found to provide excellent fluorescent effects which are vital for signal amplification by laser light pumping. In particular, the present erbium-doped, boron-free glasses may have an excited-state lifetime that is at least 8 ms in length. The emission bandwidth of the 4 I 13/2-4 I 15/2 transition is around 20 nm, and the emission cross-section at a wavelength of 1538 nm may be higher than $5 \times 10^{-25} \text{ m}^2$.

The glasses of the invention are predicated in large measure on my discovery that the B₂O₃ content in prior borosilicate glasses can be replaced with oxides of lead (PbO) and/or phosphorus (P₂O₅). When such replacement is made, the depressing effect of B₂O₃ is avoided, and the desirable properties of an erbium-doped glass are obtained. Furthermore, the new B₂O₃-free glasses possess essentially as good properties for thallium ion exchange as did the prior borosilicate glasses. This enables burying an optical waveguide in the glass by ion exchange.

The properties required for thallium ion exchange are:

1. A transformation range (T_g) below 500 °C to permit thallium ion exchange in the temperature range of 350-450 °C.
2. A sufficient amount of Na and/or K ions to exchange with thallium.
3. A ratio of K/Na ions equal to or greater than 2 to preserve the rate of exchange with thallium.
4. Good durability of the glass to withstand chemical attack during the masking and ion exchange processes.

My new glasses are capable of meeting these requirements, as well as providing the emission characteristics necessary for successful signal amplification. The glasses have a silica base, are boron-free, and must contain at least one oxide selected from Na₂O and K₂O, and at least one oxide selected from P₂O₅ and PbO. Optionally, the glasses may contain minor amounts of divalent oxides, particularly BaO and ZnO.

Alumina (Al₂O₃) is effective in broadening the erbium emission spectra at around 1.5 microns. Therefore, the glass must have an Al₂O₃ content sufficiently high to achieve this effect. Al₂O₃ also tends to improve glass durability, and thereby enable the glass to withstand chemical attack during processing. However, the Al₂O₃ content must not exceed about 4.5% to avoid a glass transformation range higher than 500 °C.

The alkali metal oxides, Na₂O and K₂O must be present to provide a glass that is ion-exchangeable with thallium ions. The oxides also serve to soften the glass, that is provide a low T_g glass. Preferably, the glasses contain both oxides with a K₂O:Na₂O ratio of at least 2:1. A ratio greater than 2:1 appears to provide optimum conditions for ion exchange with thallium. While either alkali metal oxide may be omitted from the present glasses, their total content must be within the range of 15-30 weight %. The maximum

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TABLE III

Compositions and Their Properties

Wt %	1	2	3	4	5	6	7
SiO ₂	67	54.7	55.8	55.4	38.3	55.8	54.2
Na ₂ O	6.4	5.7	5.7	5.8	4.7	5.7	0
K ₂ O	19.1	17.1	17.1	17.3	14	17	24.9
BaO	3.2	2.8	2.8	0	2.3	2.9	2.8
Al ₂ O ₃	2.1	1.9	1.9	1.9	1.5	1.9	1.8
ZnO	2.2	1.9	1.9	3.4	1.5	1.9	1.9
Li ₂ O	0	0.9	0	1	0.8	0	0
PbO	0	15	14.8	15.2	36.9	14.8	14.4
P ₂ O ₅	5	0	5	0	0	5	5
excess							
Properties							
Tg(°C)	435	416	412	416	377	405	435
nd	1.504	1.544	1.542	1.544	1.613	1.5391	1.5373
T(ms)	9.8	9	9.8	8.5	12	10	>11
Er ³⁺ (cm ³)	1.58	1.76	1.18	1.74	1.43	0.59	0.6
10E-20							
Emission	21	21	21	21	20	20	20
Bandwidth							
(nm)							
Emission	1538	1538	1538	1538	1538	1537	1537
Peak(nm)							

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FIGURE 2 is a plot showing the emission cross-section and the absorption cross-section for a silicate glass having an erbium doping level of 3.3×10^{19} atoms/cm³ and a lifetime of about 8 ms. Wavelength is plotted in nanometers (nm) on the horizontal axis, while cross-section in meters² x 10⁻²⁵ is plotted on the vertical axis. Based on these plots, a gain of 0.5 dB has been determined for a length of about 4 cm.

An optical waveguide for present purposes begins with melting a glass having a composition as defined above. A thin wafer or flat disk is formed from the melt. This may be a pressed body, or one cut from a larger body. In either case, the body is finished as required.

The glass body is then selectively coated with a mask preparatory to treatment in a molten salt bath. The selective coating is impervious to ion migration. It covers the glass surface, except for a narrow zone left exposed on the glass surface. The mask may be an oxide coating as described in United States Patent No. 3,857,689 (Koizumi et al.), or may be any other suitable resist coating.

The masked glass body is then exposed to a thallium salt bath to exchange thallium ions for sodium and/or potassium ions from the glass. The salt bath is at a temperature in the range of 350-450 °C and exposure will be for a time sufficient to form a fibre-like, ion-exchanged zone in the exposed glass surface.

The masked glass body is then exposed to an alkali metal salt bath, e.g. a KNO₃ bath, at the same temperature, to drive the thallium-ion fibre into the glass by further ion exchange. The protective mask is then removed to complete the process.

Claims

1. A glass having ion exchange properties particularly adapted to production of optical signal amplifiers operating at a wavelength of about 1.5 microns, that is free of B₂O₃, that is capable of being doped with up to 5 weight % erbium oxide, that has good spectroscopic properties and that has a base glass composition consisting essentially of, on an oxide basis as calculated in weight percent,

SiO ₂	38-67	Al ₂ O ₃	1.5-4.5
Na ₂ O	0-20	ZnO	1.5-8
K ₂ O	0-25	Li ₂ O	0-1
Na ₂ O + K ₂ O	15-30	PbO	0-37
BaO	0-7	P ₂ O ₅	0-5
		P ₂ O ₅ + PbO	5-37

2. Glass in accordance with claim 1 having a base composition consisting essentially of, on an oxide basis as calculated in weight percent

SiO ₂	52-56	ZnO	1.5-8
K ₂ O	0 - 25	Li ₂ O	0 - 1
Na ₂ O	0-20	PbO	10-15
Na ₂ O + K ₂ O	18 - 26	P ₂ O ₅ excess	0 - 5
K ₂ O:Na ₂ O	2-3.3:1	P ₂ O ₅ + PbO	15 - 20
BaO	0 - 3		
Al ₂ O ₃	1.5 - 4.5		

3. Glass in accordance with claims 1 or 2 having a transformation temperature below 500 °C whereby thallium ion exchange can occur at a temperature in the range of 350-450 °C.

4. Glass in accordance with claims 1, 2 or 3 wherein the composition contains both K₂O and Na₂O, the total of these oxides being 15-30% by weight.

5. Glass in accordance with claim 4 wherein the K₂O:Na₂O ratio is at least 2:1.

6. Glass in accordance with any one of claims 1-5, wherein the glass composition is modified within a selective area by at least partial replacement of potassium and/or sodium ions by thallium ions.

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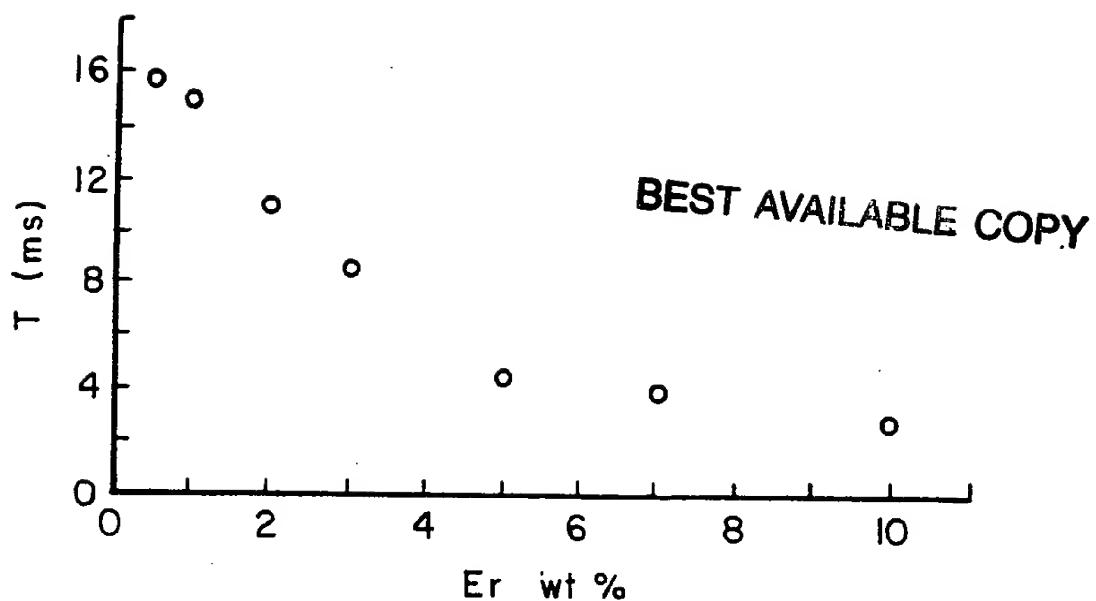


Fig. 1

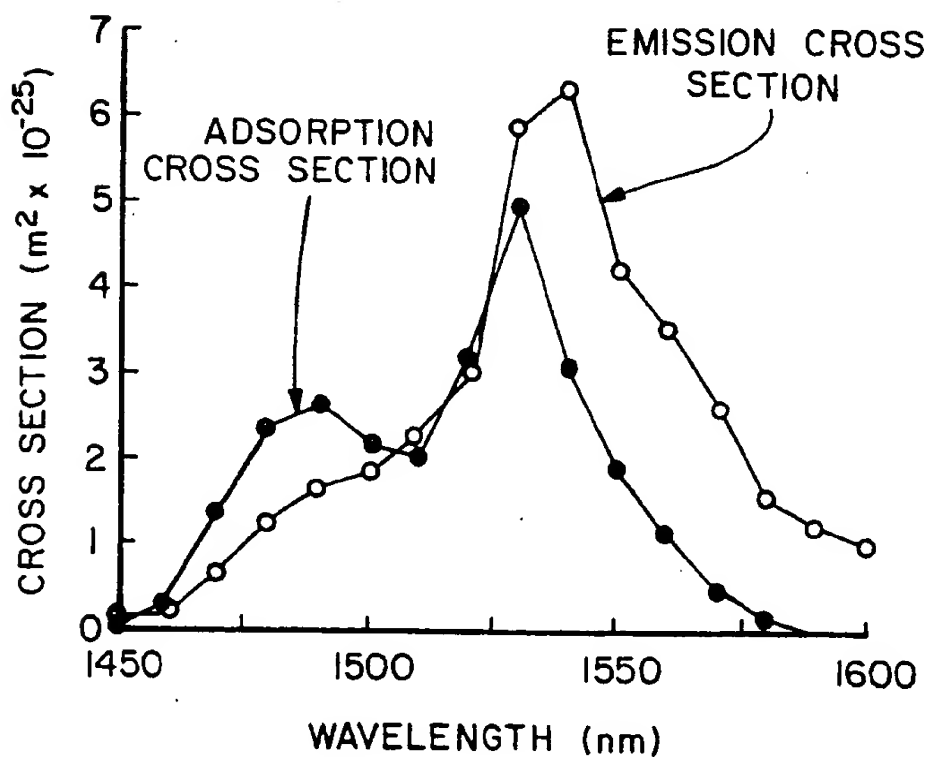


Fig. 2

